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## (54) WATER-BASED METALLIC INK COMPOSITION

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a water-based metallic ink composition capable of suppressing a viscosity change of an ink and excellent in stability of the viscosity with time. SOLUTION: This ink composition contains a metal powder pigment, a pigment, an anionic polymer, a pH stabilizer and a thickener and the pH of the ink composition is regulated to 8.0-10. The anionic polymer is selected from an acrylic resin, a styrene-acrylic copolymer, polymaleic acid, a styrene-maleic acid copolymer, polyvinylpyrrolidone, an ester-acrylic copolymer and a resin having carboxyl groups. The pH stabilizer includes a benzotriazole or its derivative.

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#### CLAIMS

[Claim(s)]

[Claim 1] The water metallic ink constituent characterized by being an ink constituent containing a metal-powder pigment, a pigment, and an anionic macromolecule, and pH being 8.0-10.

[Claim 2] The water metallic ink constituent according to claim 1 with which the aforementioned anionic macromolecule was chosen from acrylic resin, a styrene-acrylic copolymer, a polymer lane acid, the styrene-maleic-acid copolymer, the polyvinyl pyrrolidone, the ester-acrylic copolymer, and the resin that has a carboxyl group and which is a kind at least.

[Claim 3] Furthermore, the water metallic ink constituent containing pH stabilizer according to claim 1 or 2.

[Claim 4] A water metallic ink constituent given in the claim 1 whose pH stabilizer is a benzotriazol or its derivative, or one term of 3.

[Claim 5] Furthermore, a water metallic ink constituent given in the claim 1 containing a thickener, or one term of 4.

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#### ABSTRACT:

PROBLEM TO BE SOLVED: To obtain a water-based metallic ink composition capable of suppressing a viscosity change of an ink and excellent in stability of the viscosity with time.

SOLUTION: This ink composition contains a metal powder pigment, a pigment, an anionic polymer, a pH stabilizer and a thickener and the pH of the ink composition is regulated to 8.0-10. The anionic polymer is selected from an acrylic resin, a styrene-acrylic copolymer, polymaleic acid, a styrene-maleic acid copolymer, polyvinylpyrrolidone, an ester-acrylic copolymer and a resin having carboxyl groups. The pH stabilizer includes a benzotriazole or its derivative.

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## **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[The technical field to which invention belongs] this invention relates to a still more detailed water metallic ink constituent with the good stability of viscosity with the passage of time about a water metallic ink constituent.

[0002]

[Description of the Prior Art] Conventionally, in the water metallic ink constituent used as an object for ball-points etc., a metal-powder pigment, and a pigment and its dispersant are used. As a dispersant of this pigment, the anionic macromolecule is used in many cases. [0003]

[Problem(s) to be Solved by the Invention] However, the anionic macromolecule as such a pigment agent may condense and deposit, and viscosity change (for example, viscosity rise) of ink may be caused. Moreover, a metal-powder pigment (especially aluminium-powder pigment) tends to become ion in ink, and pH of ink changes with the ion components produced from the metal-powder pigment. If pH of ink falls especially, the anionic macromolecule in ink will condense or deposit, and the viscosity of ink will change. In addition, viscosity change of the ink at the time of the anionic macromolecule in ink condensing or depositing is thickening in many cases.

[0004] That is, if the stability of the viscosity of ink with the passage of time is low if the ink containing the anionic macromolecule is used, and saved over a long period of time, it may thicken and note nature may fall.

[0005] The purpose of this invention is to offer the water metallic ink constituent excellent in the stability of viscosity with the passage of time.

[Means for Solving the Problem] As a result of repeating research wholeheartedly, when pH of ink was adjusted in the metal-powder pigment, the pigment, and the water metallic ink constituent containing the anionic macromolecule, this invention persons find out that viscosity change of the ink under preservation can be suppressed or prevented, and came to complete this invention. That is, invention of a claim 1 is an ink constituent containing a metal-powder pigment, a pigment, and an anionic macromolecule, and is a water metallic ink constituent characterized by pH being 8.0-10.

[0007] Since the water metallic ink constituent of this invention is adjusting pH of ink to the specific value, even if the anionic macromolecule as a pigment agent is used for it, it can suppress or prevent during preservation that ink causes viscosity change. Since it is anionic, an anionic macromolecule causes condensation and a deposit as ink is acidity or weak alkalinity (when pH is less than eight), or it is easy to start it. Moreover, even if ink is alkaline, in a strong base, a metal-powder pigment is changed into a metaled hydroxide (especially an aluminium-powder pigment is an aluminum hydroxide) (when pH exceeds 10), and the metallic

luster of ink may disappear. Therefore, since the ink of this invention has specific pH, the viscosity of ink is controlled over a long period of time, and the stability of the viscosity of ink with the passage of time is excellent. Moreover, the stability of a metal-powder pigment can also be held for a long period of time.

[0008] If the ranges of pH are 8.0-10 in a water metallic ink constituent, the knowledge that the stability of viscosity with the passage of time is excellent is not acquired conventionally, and an indication is not carried out, either. Therefore, this invention is new invention, and since the stability of viscosity with the passage of time can be raised easily, it is very useful invention. [0009] On the occasion of adjustment of pH of ink, basic compounds, such as a basic inorganic compound (a "inorganic base" may be called hereafter) and a basic organic compound (a "organic base" may be called hereafter), can be used, for example. [0010] in this invention, it was chosen from acrylic resin, a styrene-acrylic copolymer, a polymer lane acid, the styrene-maleic-acid copolymer, the polyvinyl pyrrolidone, the esteracrylic copolymer, and the resin that has a carboxyl group as the aforementioned anionic macromolecule -- a kind can be used at least

[0011] It is desirable to use pH stabilizer in the aquosity metallic ink constituent of this invention. If pH stabilizer is used, even if a metal-powder pigment, especially an aluminium-powder pigment ionize and it separates in prolonged preservation etc., the change of pH (fall of pH) in ink can be inhibited or suppressed. Therefore, if pH stabilizer is used, even if it saves ink over a long period of time, change of the viscosity of ink can be suppressed or prevented. [0012] In this invention, a benzotriazol or its derivative can be suitably used as a pH stabilizer. [0013] Moreover, in the aquosity metallic ink constituent of this invention, the aquosity metallic ink constituent which the thickener contains is further contained in a desirable mode. [0014]

[Embodiments of the Invention] the aquosity metallic ink constituent of this invention -- pH -- 8.0-10 -- it is 8.5-9.5 preferably If pH of ink is too lower than 8.0, an anionic macromolecule will become easy to cause condensation or a deposit. On the other hand, if pH is too higher than 10, a metal-powder pigment is changed into a hydroxide, and the metallic luster of ink may disappear.

[0015] In order to hold pH of ink in the aforementioned range, it is desirable to set up pH at the time of ink manufacture more highly a little from the aforementioned range. Thus, if pH at the time of ink manufacture is set up more highly a little, even if pH falls a little during ink preservation, the range of pH with the high stability of the viscosity of ink with the passage of time can be held. Therefore, in this invention, it is desirable 8.3-10, and to choose pH at the time of ink manufacture from the range of 8.8-9.8 preferably. As for especially pH at the time of ink manufacture, in this invention, about nine are usually desirable.

[0016] (Basic compound) Especially as a basic compound used for pH adjustment of ink, it is not restricted but the basic compound currently used in common use can be used. As a basic compound, an inorganic base and an organic base can be used, for example. A basic compound is independent, or it can be used, combining it two or more sorts. In addition, as a basic compound, an inorganic base is used in many cases.

[0017] The hydroxide of alkaline earth metal, such as a hydroxide of alkali metal, such as a sodium hydroxide and a potassium hydroxide, and a calcium hydroxide, etc. is contained in an inorganic base. As an inorganic base, the hydroxide of alkali metal, especially a sodium hydroxide can be used suitably. Moreover, as an organic base, monochrome, such as monochrome, such as a trimethylamine and a triethylamine, JI or alkylamine, trimethano RUAMIN, and a triethanolamine, JI, or a TORIARU call amine can be used suitably, for example.

[0018] Especially the amount of the basic compound used is not restricted, but can be suitably chosen according to pH of the ink made into the kind of other components, its amount used,

and the purpose. More specifically, the amount of the basic compound used is an amount from which pH at the time of preparing ink becomes 8.3 to about ten.

[0019] (Metal-powder pigment) What has metallic luster can be used as a metal-powder pigment, and what has the high dispersibility over water is desirable. As a metal-powder pigment, you may be a leafing type and may be a non leafing type. Especially as a metal-powder pigment, it is not restricted, for example, a brass powder pigment, an aluminium-powder pigment, especially an aluminium-powder pigment can be used suitably. [0020] As an aluminium-powder pigment, specifically Tradename:ARUPESUTOWJP-U75C (Toyo Aluminium K.K. make), Tradename: ARUPESUTO WE1200 (Toyo Aluminium K.K. make), tradename:ARUPESUTO WXM7675 (Toyo Aluminium K.K. make), Tradename: ARUPESUTO WXM0630 (Toyo Aluminium K.K. make), tradename:1110W (Showa Aluminum Corp. make), Tradename: 2172SW (Showa Aluminum Corp. make), tradename:AW-808C (Asahi Chemical Industry Co., Ltd. make), tradename:AW-7000R (Asahi Chemical Industry Co., Ltd. make), etc. can be illustrated.

[0021] As a brass powder pigment, tradename:BS-605 (Toyo Aluminium K.K. make), tradename:BS-607 (Toyo Aluminium K.K. make), the tradename:bronze powder P-555 (product made from Nakajima Metallic foil Powder Industry), the tradename:bronze powder P-777 (product made from Nakajima Metallic foil Powder Industry), etc. are mentioned, for example.

[0023] A metal-powder pigment is independent, or it can be used, combining it two or more sorts. The amount of the metal-powder pigment used is 4 - 15 % of the weight preferably three to 30% of the weight for example, to the ink constituent whole quantity. Metallic luster may not be discovered in too little [ the amount of the metal-powder pigment used ]. On the other hand, since a solid content increases that it is excessive, influence arises to the viscosity and the fluidity of an ink constituent, and note nature etc. falls by elevation and a fluid fall of viscosity. [0024] (Pigment) As a pigment, to water color ink, if dispersibility is good, it can be especially used without a limit. Specifically as a pigment, inorganic pigments, such as organic pigments, such as a phthalocyanine system, the Indanthrene system, an azo system, a Quinacridone system, an anthraquinone system, a dioxane system, an indigo system, a thioindigo system, peri non \*\*, a perylene system, an iso indoline system, and an azomethine system, titanium oxide, a zinc white, an iron oxide, and carbon black, a fluorescent pigment, the pigment which colored the plastics pigment by the pigment or the color, etc. are mentioned, for example. An organic pigment and an inorganic pigment are contained in a desirable pigment. [0025] A pigment is independent, or it can be used, combining it two or more sorts. The

amount of the pigment used is 1 - 10 % of the weight preferably 0.05 to 15% of the weight for example, to the ink constituent whole quantity. When coloring is low in too little [ the amount of the pigment used ] and it combines with a metal-powder pigment, the paint film of a metallic tone may not be obtained. On the other hand, since a solid content increases that it is excessive, influence arises to the viscosity and the fluidity of an ink constituent, and note nature etc. falls by elevation and a fluid fall of viscosity.

[0026] (Anionic macromolecule) The anionic macromolecule is used as a resin for pigment-content powder for making the coat of a hand easy to form, in order to prevent condensation of a pigment and to plan distributed stability. An anionic macromolecule is independent, or it can be used, combining it two or more sorts.

[0027] Specifically as an anionic macromolecule, the resin which has acrylic resin, a styreneacrylic copolymer, a polymer lane acid, a styrene-maleic-acid copolymer, a polyvinyl pyrrolidone, an ester-acrylic copolymer, and a carboxyl group is mentioned. A kind of resin chosen from acrylic resin, the styrene-acrylic copolymer, the ester-acrylic copolymer, the polymer lane acid, and the styrene-maleic-acid copolymer is contained in a desirable anionic macromolecule at least. Moreover, the denaturation object of a resin or the above-mentioned resin neutralized with alkali metal etc. is also contained.

[0028] Especially the amount of the anionic macromolecule used is not limited, for example, is 0.3 - 1.5 % of the weight still more preferably 0.1 to 2% of the weight preferably 0.01 to 5% of the weight to the ink constituent whole quantity. If there is too little amount of the anionic macromolecule used, it will be easy to produce flocking settling of a pigment, and on the other hand, if many [ too ], viscosity will become high too much and note nature and a printability will fall.

[0029] (pH stabilizer) It is desirable to use pH stabilizer in this invention. This can control pH of ink over a long period of time, if pH stabilizer which has buffer action (buffer action over pH change) is used. Therefore, in a metal-powder pigment, even if an ion component separates, the change of pH of ink can be suppressed or prevented by pH stabilizer.

[0030] As a pH stabilizer, a 1H-benzotriazol or its derivative can be illustrated, for example. As a derivative of a 1H-benzotriazol, the salts (sodium salt, an ammonium salt, silver salt, etc.) of the 4-methyl -1, H-benzotriazol, the 5-methyl -1, H-benzotriazol, 4-chloro -1, H-benzotriazol, 5-chloro -1, H-benzotriazol, and benzotriazol butyl ester etc. can be illustrated, for example. In addition, a benzotriazol (1H-benzotriazol) or its derivative is contained in desirable pH stabilizer.

[0031] When using pH stabilizer, it is independent, or two or more sorts can be used, combining. It is not restricted especially about the amount of pH stabilizer used. For example, in the case of a benzotriazol (1H-benzotriazol) or its derivative, it is 0.05 - 0.15 % of the weight still more preferably 0.01 to 1.0% of the weight preferably 1.5 or less % of the weight to the ink constituent whole quantity. Buffer action falls as too little [ the amount of pH stabilizer used ]. On the other hand, pH stabilizer etc. may not dissolve that it is excessive.

[0032] In addition, pH stabilizers, such as a benzotriazol or its derivative, can also have a function as a rusr-proofer.

[0033] (Thickener) The aquosity metallic ink constituent of this invention can be made to contain a thickener if needed. If natural polysaccharide is especially used as a thickener, the ink which has \*\*\*\*\*\* plastics nature, and the so-called gel type of ink can be obtained. [0034] As natural polysaccharide, the system polysaccharide from a microorganism or its derivative, water-soluble vegetable system polysaccharide or its derivative, water-soluble animal system polysaccharide, or its derivative can be used.

[0035] As the system polysaccharide from a microorganism, or its derivative, a pullulan, xanthan gum, WERANGAMU, ram ZANGAMU, a SAKUSHINO glucan, a dextran, etc. can be illustrated, for example.

[0036] water-soluble vegetable system polysaccharide or its derivative -- for example, TORAGANSHIGAMU, Cyamoposis Gum, and a tare -- gum, locust bean gum, a ghatti gum, arabinogalactan gum, gum arabic, KUISU seed gum, pectin, starch, a psyllium seed gum, a carrageenan, an alginic acid, an agar, etc. are contained Gelatin, casein, etc. are contained in water-soluble animal system polysaccharide or its derivative.

[0037] As desirable natural polysaccharide, the system polysaccharide from a microorganism or its derivative especially xanthan gum, WERANGAMU, ram ZANGAMU, etc. are mentioned. [0038] A thickener is independent, or it can be used, combining it two or more sorts. The amount of the thickener used is 0.3 - 1.5 % of the weight still more preferably 0.1 to 2% of the weight preferably 0.01 to 4% of the weight to the ink constituent whole quantity, when preparing the so-called gel type of ink. If there is too little amount of the thickener used, the dispersibility of a metal-powder pigment may fall and a metal-powder pigment may sediment. if many [ on the other hand / too ] -- the viscosity of an ink constituent -- high -- becoming -- note

nature -- printing proper \*\*\*\*\* is carried out

[0039] (Resin for coloring) In this invention, in order to raise the fixing nature of the pigment dispersing element of a metal-powder pigment for grant of the hydrophilic property to the improvement metallurgy group powder pigment of the dispersibility of a metal-powder pigment, the resin for coloring can be used because of prevention of the ion elution from a metal-powder pigment, and the coat formation promotion in a hand.

[0040] As a resin for coloring, a cellulosic, cyclodextrin or its derivative, water-soluble soybean polysaccharide, or its derivative is mentioned, for example. The resin for coloring is

independent, or it can be used, combining it two or more sorts.

[0041] As a cellulosic, a methyl cellulose, a hydroxyethyl cellulose, hydroxypropylcellulose, the hydroxypropyl methylcellulose, a hydroxypropyl ethyl cellulose, carboxymethyl-cellulose, or its salts (sodium salt, ammonium salt, etc.) are mentioned, for example. A carboxymethyl cellulose or its salts (sodium salt, ammonium salt, etc.) are preferably contained in a carboxymethyl cellulose or its salt, a hydroxyethyl cellulose, and a pan at a desirable cellulosic. These cellulosics especially a carboxymethyl cellulose, or its salt can discover the operation which raises the hydrophilic property to a metal-powder pigment, especially an aluminium-powder pigment.

[0042] although especially the number average molecular weight of a cellulosic is not restricted -- 8,000-400,000 -- it can choose from about 10,000 to 100,000 range preferably [0043] As cyclodextrin or its derivative, alpha-cyclodextrin, beta-cyclodextrin, gammacyclodextrin or these alkyl derivatives, malto sill cyclodextrin, a glucosyl SUKURO dextrin, etc. are mentioned, for example. The methyl derivative of cyclodextrin, such as 2, 6-dimethyl-betacyclodextrin, 2 and 3, and 6-TORIMECHIRU-beta-cyclodextrin, etc. is contained in the alkyl derivative of cyclodextrin (alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin). [0044] it was chosen from alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin, and these derivatives as desirable cyclodextrin or its derivative -- a kind is mentioned at least and the mixture (for example, mixture of alpha-cyclodextrin, beta-cyclodextrin, and gammacyclodextrin) of alpha-cyclodextrin, alpha-cyclodextrin, and beta-cyclodextrin and/or gammacyclodextrin can be illustrated still more preferably The content of alpha-cyclodextrin is 30 % of the weight or more (preferably 50 % of the weight or more) for example, to the mixture whole quantity that the mixture (mixture of alpha-cyclodextrin, and beta-cyclodextrin and/or gammacyclodextrin) of this cyclodextrin should just contain alpha-cyclodextrin. [0045] As water-soluble soybean polysaccharide or its derivative, it is formed from the sugar of a galactose, arabinose, a galacturonic acid, a rhamnose, a xylose, a fucose, a glucose, and varieties, and the thing of the structure which the galactan and the arabinan combined with the ram galacturonic-acid chain is mentioned. More specifically as water-soluble soybean polysaccharide or its derivative, it is tradename: SOYAFAIBU. S-DN (FUJI OIL [ Co., Ltd. ] make), tradename:SOYAFAIBU S-LN (FUJI OIL [ Co., Ltd. ] make), a tradename: SOYAFAIBU S-LN1 (FUJI OIL [ Co., Ltd. ] make), a tradename: SOYAFAIBU S-DA100 (FUJI OIL [ Co., Ltd. ] make), a tradename: SOYAFAIBU S-LA200 (FUJI OIL Co., Ltd. make) etc. can be used. [0046] The amount of the resin for coloring used is 0.3 - 20 % of the weight preferably for example, to the ink constituent whole quantity 40 or less (for example, 0.01 - 40 % of the weight) % of the weight. If there is too little amount of the resin for coloring used, the fixing nature of a coloring agent to a metal-powder pigment will fall, and the coloring concentration of a paint film will fall. On the other hand, if many [ too ], condensation may take place between metal-powder pigments, and influence (viscosity elevation) may arise to viscosity. [0047] (Water-soluble organic solvent) Water-soluble organic solvents, such as the watersoluble organic solvent currently used in common use if needed for the purpose of dryness prevention or the anti-freeze at the time of low temperature, for example, glycols, glycol ethers, and carbitols, can be used for the aquosity metallic ink constituent of this invention. More

specifically as a water-soluble organic solvent, carbitols, such as glycol ethers, such as glycols, such as ethylene glycol, a diethylene glycol, and a propylene glycol, and an ethylene glycol monomethyl ether, and the diethylene-glycol monomethyl ether, a glycerol, a trimethyl propane, etc. are mentioned, for example.

[0048] Especially as amount of the water-soluble organic solvent used, it is not restricted, for example, is about 5 - 20 % of the weight preferably to the ink constituent whole quantity 40 or less (for example, 1 - 40 % of the weight) % of the weight. If there is too little amount of the water-soluble organic solvent used, it will be easy to dry an ink constituent, blinding etc. will arise, and note nature will fall. On the other hand, when many [ too ], there is a bird clapper that it is hard to dry after a note.

[0049] (Water), of course, water is contained in the aquosity metallic ink constituent of this invention. If it is water (for example, ion exchange water, distilled water, etc.) currently used in common use as water, it can use satisfactory at all. Especially the amount of the water used is not restricted, but can be suitably chosen according to the kind of other components (metal-powder pigment, pigment, anionic macromolecule, basic compound, and pH stabilizer, a thickener, water-soluble organic solvent, etc.) or its amount used, the viscosity of the ink constituent made into the purpose, etc. The amount of the water used can be chosen from about 1 - 95% of the weight of the range to the latus range, for example, the ink constituent whole quantity. The amount of the desirable water used is about 20 - 90 % of the weight. [0050] In addition, a moisture powder type resin can be used together with the aforementioned anionic macromolecule in the aquosity metallic ink constituent of this invention. As a moisture powder type resin, an acrylic emulsion, a vinyl acetate system emulsion, an urethane system emulsion, a styrene-butadiene emulsion, etc. are mentioned.

[0051] (Additive etc.) In the water-color-ink constituent of this invention, additives other than each above-mentioned component, such as lubricant, a rusr-proofer, an antisepsis antifungal agent, a thickener stabilizing agent, and various surfactants, can be added if needed. As lubricant, a polyoxyethylene alkali-metal salt, dicarboxylic-acid amides (maleic-acid monoamide etc.), phosphoric ester, an N-oleyl sarcosine salt, etc. are mentioned, for example. As a rusr-proofer, a dicyclohexyl ammonium nitrate etc. is mentioned, for example. As an antisepsis antifungal agent, a BENZO iso thiazoline system, a pentachlorophenol system, cresol, etc. are mentioned, for example. As a thickener stabilizing agent, the sodium salt of carboxylic acids, such as sodium salt of a benzoic acid, etc. is mentioned, for example, [0052] the viscosity for which the viscosity is used in common use in the aguosity metallic ink constituent of this invention when preparing the so-called gel type of ink, i.e., a pigment, -- not sedimenting -- note nature and printing -- if it is the viscosity for which it was suitable proper, it will not be restricted especially As for the viscosity of the so-called gel type of ink, in the aquosity metallic ink constituent of this invention, it is preferably desirable in 20 degrees C to choose from the range of 3,000-15,000cps 2,000-40,000cps. In addition, viscosity is measured in cone:3-degreeR14 cone, rotational frequency:0.5rpm, and temperature:20 degree C using a ELD type viscometer.

[0053] (The manufacture method) It mixes by the method of common use of the aforementioned component (a metal-powder pigment, a pigment, an anionic macromolecule, a basic compound, water, and the need are accepted, and them are a resin for pH stabilizer, thickener, resin for coloring, water-soluble organic-solvent, and pigment-content powder, an additive, etc.), and the water-color-ink constituent of this invention can be prepared. More specifically, a pigment is dissolved with water, a solvent, etc., it distributes, and a pigment dispersing element is prepared. And water, the water-soluble organic solvent, and a metal-powder pigment are mixed, a metal-powder pigment dispersing element is prepared, after throwing the resin for coloring into the aforementioned metal-powder pigment dispersing element, making it stick to a metal-powder pigment and throwing in a thickener, an additive,

etc. the aforementioned pigment dispersing element and if needed if needed, pH adjustment can be performed using a basic compound and the water color ink of a metallic tone can be prepared.

[0054] As methods, such as distribution performed on the occasion of manufacture of an aquosity metallic ink constituent, degassing, and filtration, the method of common use is employable.

[0055] The aquosity metallic ink constituent of this invention has a small viscosity change over a long period of time. Therefore, the viscosity of an ink constituent is controllable to proper viscosity according to a use. Therefore, it can control to the viscosity suitable for uses (a note, printing, etc.), and, moreover, proper viscosity can be held for a long period of time. [0056] Therefore, the aquosity metallic ink constituent of this invention is useful as water color ink used in the ink for record (for example, the ink for printing, a copying ink, ink for ink-jet record, etc.), or a paint related field. [0057]

[Example] Hereafter, although this invention is explained more to a detail based on an example and the example of comparison, this invention is not limited to these examples. [0058] (Example of manufacture of pigment base \*\*) Coloring agent (a copper phthalocyanine blue, tradename: first gene blue TGR, Dainippon Ink & Chemicals, Inc. make), Dissolved the resin for pigment-content powder (a styrene-acrylic copolymer, the tradename: JON krill J683, Johnson polymer company make, about 8,000 weight average molecular weight) in ion exchange water at a rate of a copper phthalocyanine blue / styrene-acrylic copolymer =5 / 1 (weight ratio), supplied the triethylamine, the ball mill was made to distribute, and the pigment dispersing element of 0.08 micrometers of mean particle diameters and 10 % of the weight of solid-content concentration was prepared. Hereafter, this pigment dispersing element is called pigment base \*\*.

[0059] (Example of manufacture of pigment base \*\*) Coloring agent (iso indoline, tradename:dolphin gin yellow 2RLT, product made from tiba speciality KEMIKARUZU), the resin for pigment-content powder (a styrene-acrylic copolymer, the tradename:JON krill J683, Johnson polymer company make, about 8,000 weight average molecular weight) -- iso -- indoline / styrene-acrylic copolymer =5 / 1 (weight ratio) came out comparatively, and dissolved in ion exchange water, supplied the triethylamine, the ball mill was made to distribute, and the pigment dispersing element of 0.15 micrometers of mean particle diameters and 10 % of the weight of solid-content concentration was prepared Hereafter, this pigment dispersing element is called pigment base \*\*.

[0060] (Examples 1-8) In each example, it blended at a rate (each loadings of the various components in Table 1 are weight %) shown in Table 1, respectively, pH adjustment was performed, and the ink constituent was prepared. Specifically, the aquosity metallic ink constituent concerning examples 1-8 is ion exchange water and a glycerol (following.). And it calls "organic-solvent \*\*", into the mixed liquor of a propylene glycol ("organic-solvent \*\*" is called hereafter), a metal-powder pigment (an aluminium-powder pigment, tradename: WXM0630, Toyo Aluminium K.K. make) is stirred at a room temperature (20-25 degrees C) for 1 hour. After making it distribute, threw in the resin for coloring (the carboxymethyl-cellulose and tradename: cello gene PR, the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, about 47,000 to 54,000 number average molecular weight), stirred for further 1 hour, the resin for coloring was made to stick to a metal-powder pigment, and it coated. Pigment base \*\* or \*\* is added and it stirs at a room temperature (20-25 degrees C) for 1 hour, and the coloring agent was made to adsorb and it was made to color it this dispersing element on a metalpowder pigment. A thickener (thickener \*\*, \*\*, or \*\*), pH stabilizer (pH stabilizer \*\* or \*\*), and additives, such as an antisepsis antifungal agent, lubricant, and a thickener stabilizing agent, were thrown into the dispersing element of this colored metal-powder pigment, further, at the

room temperature (20-25 degrees C), it stirred for 1 hour and water color ink was obtained. In this ink, pH of ink was adjusted using a sodium hydroxide as a basic compound, pH of ink was adjusted to 9, and the water color ink of the metallic tone of blue or yellow was obtained. [0061] In addition, as a thickener, ram ZANGAMU (tradename: K 7C233, Sansho [ Co., Ltd. ] Co., Ltd. make) was used as thickener \*\* as WERANGAMU (tradename: K one A96, Sansho [ Co., Ltd. ] Co., Ltd. make) and thickener \*\* as xanthan gum (tradename: KELZAN, Sansho [ Co., Ltd. ] Co., Ltd. make) and thickener \*\*. As a pH stabilizer, the tolyl triazole (4-methylbenzotriazol) was used as benzotriazol and pH stabilizer \*\* as pH stabilizer \*\*. [0062] Moreover, as an antisepsis antifungal agent, 1 and 2-BENZO iso thiazoline-3-ON (tradename: pro KUSERU GXL, the product made from Hoechst Composition) was used. The sodium salt of a benzoic acid was used as a thickener stabilizing agent, using the maleic-acid monoamide as lubricant.

[0063] (Example 1 of comparison) In the example 1 of comparison, it blended at a rate (each loadings of the various components in Table 2 are weight %) shown in Table 2, and aquosity metallic ink was prepared like the aforementioned example except performing pH adjustment. More specifically on the occasion of manufacture of the ink concerning the example 1 of comparison, the water color ink of a blue metallic tone was prepared, without adjusting pH. [0064] (Example 2 of comparison) In the example 2 of comparison, it blended at a rate (each loadings of the various components in Table 2 are weight %) shown in Table 2, and manufacture of aquosity metallic ink was tried like the aforementioned example except the value of pH in pH adjustment. Although it more specifically adjusted on the occasion of manufacture of the ink concerning the example 2 of comparison so that pH of ink might be set to 11 using a sodium hydroxide, since gas (hydrogen gas etc.) occurred and it milked from the inside of ink while having left it for a while, aquosity metallic ink was not able to be prepared. [0065]

[Table 1]

					表 1				
Į		実 施 例							
		1	2	3	4	5	6	7	_ 8
金属粉酸	<b>(*)</b>	5	5	5	5	5	5	ឥ	₽.
顔料ベース①		30	30			80			30
顔料ベース②		Γ		30	30		30	30	
着色用樹脂		2	2	2	2	2	2	2	2
増粘剤①		0.5	0.5						
増粘剤②				0.4	0.4	l		0.4	
增粘剤③	)					0.4	0.4		0.4
pH安定	<b>利①</b>	0.05		0.1		0.15	L		
p H安定	剤②		0.1		0.15	L	0.1		
有機溶剤	有機溶剤①		2.5	2.5	2.5	2.5	2.5	2.5	2.5
有機溶剤②		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
防腐防黴剤		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
潤滑剤		1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
增粘剤安定化剤		0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
水		56.55	56.5	56.5	56.0	56.0	56.5	56.7	56.7
pН	保存前	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
	30日	8.8	8.9	8.7	8.7	8.9	8.8	8.0	8.2
	60Ħ	8.6	8.8	8.5	8.6	8.7	8.8	7.5	7.7
粘度	30 H	0	0	0	0_	0	0	Δ	0
	60月	0	0	0	0_	0	0	×	×
筆記性	30月	0	0	0	0_	_ 0	0	Δ	0
	60B	0	0	0	0	0	0	×	×

[0066] [Table 2]

	∄	€ 2 _		
		比	較 例	
•	_	1	2	
金属粉餌	料 _	5	5	
顔料べー	ス①	90	İ	
顔料べー	ス②	T	30	
着色用樹	脂	2	2	
増粘剤①	)	0.5		
増粘剤②	)		ļ	
增粘剤③			0.4	
p H安定	剤①	<u> </u>		
pH安定	剤②	0.1	0.1	
有機溶剤	(I)	2.5	2.5	
有機溶剤	12	1.5	1.5	
防腐防御	剤	0.1	0.1	
潤滑剤		1.2	1.2	
増粘剤安	定化剤	0.6	0.6	
水		56.5	56.6	
На	保存前	7.7	11.0	
	30₽	7.3		
	60B	7.0		
粘度	30F	×		
[	60日	\	<u> </u>	
笨記性	30月	×		
	60日			

[0067] (Evaluation of an ink constituent) About the aquosity metallic ink constituent concerning examples 1-8 and the example 1 of comparison, the following pH examinations, a viscosity stability test, and the writing sex test were performed, and evaluation of pH of ink, viscosity, and note nature was performed.

[0068] (pH examination) The aquosity metallic ink constituent obtained in examples 1-8 and the example 1 of comparison was put into the polypropylene container, was sealed, and was left or saved for 30 days and for 60 days at 50 degrees C, respectively. And for 30 days, after preservation, for 60 days, when pH after preservation was investigated, the result shown in the column of "pH" in Table 1 or 2 was obtained before preservation. In addition, pH after preservation was shown in the column on "the 30th" for 30 days, and pH before preservation showed pH after preservation to the column "before preservation" for 60 days at the column on "the 60th"

[0069] (Viscosity stability test) The aquosity metallic ink constituent obtained in examples 1-8 and the example 1 of comparison is put into a polypropylene container, respectively, and is sealed, and it is 50 degrees C. Leaving or saving for 30 days and for 60 days, for 30 days, the preservation rear stirrup investigated the viscosity rate of change (viscosity x100 before the viscosity/neglect after neglect) of the ink constituent after preservation for 60 days, and evaluated the viscosity rate of change of an ink constituent by the following criteria. The result is shown in the column of "viscosity" of Table 1 or 2. In addition, the viscosity rate of change about the preservation back showed the viscosity rate of change about the preservation back to the column on "the 30th" for 60 days for 30 days at the column on "the 60th." Moreover, viscosity was measured with the ELD type viscometer on cone:3-degreeR14 cone, rotational frequency:0.5rpm, and temperature:20 degree C conditions.

O: -- less than [ 50% of less than 10% / of rate of change / \*\*:rate of change ] x: -- 50% or more of rate of change [0070] (Writing sex test) The ink hold section was filled up with the aquosity metallic ink constituent obtained in examples 1-8 and the example 1 of comparison, respectively, centrifugal separation removed the foam in ink, and the test sample of a ball-point was produced. After turning the nib up and saving this test sample for 60 days for 30 days at

50 degrees C at a thermostatic chamber, viewing estimated the writing state or the hand on the following criteria, and note nature was evaluated. The result was shown in the column of the "note nature" of Table 1 or 2. In addition, the note nature about the preservation back showed the note nature about the preservation back to the column on "the 30th" for 60 days for 30 days at the column on "the 60th." In addition, the ink hold section for ball-points which consists of a hollow shaft cylinder made from polypropylene which formed successively nickel-silver ball-point chips (quality of the material: cemented carbide of a ball) at the end as the ink hold section was used.

O: -- xwith great-difference[ preservation before and ]-less \*\*:skip: -- a note is impossible [0071] (Evaluation result) With the water metallic ink constituent concerning examples 1-6, at 50 degrees C, after leaving it for 30 days and for 60 days, pH is kept or more at 8.0. Moreover, there is almost no change of viscosity and note nature is not failing further, either. In the water metallic ink constituent concerning examples 7-8, although viscosity and note nature are almost changeless compared with preservation before, while pH after neglect was kept or more at 8.0 for 30 days at 50 degrees C, and, as for after neglect, pH fell less than to 8.0 for 60 days, viscosity increased and the note became impossible [viscosity]. On the other hand, in the water metallic ink constituent concerning the example 1 of comparison, pH at the time of ink manufacture was less than 8.0, and it was 50 degrees C, and even if it was after preservation for 30 days, viscosity increased and a note was not completed. [0072] That is, in the water color ink concerning examples 1-8, pH at the time of ink manufacture is about nine, and since pH is in the range of 8.0-10, pH after preservation is held or more by 8.0 for 30 days in 50 degrees C. In the water color ink concerning especially the examples 1-6, since pH stabilizer is contained, even if it is 50 degrees C and is after preservation for 60 days, pH is kept or more at 8.5, a change of pH is very low and pH is maintained at simultaneously regularity. On the other hand, since pH stabilizer is included, although pH after preservation is seldom falling as compared with preservation before for 30 days in the water metallic ink constituent concerning the example 1 of comparison which has not carried out pH adjustment, pH at the time of ink manufacture is less than 8.0 (being 7.7 in detail), and notes of after preservation cannot be thickened and taken as compared with preservation before for 30 days.

[0073] Therefore, if pH of ink is set to 8.0-10, viscosity of ink can be made stability, and viscosity change of ink can be suppressed or prevented. Especially the ink constituent using pH stabilizer is continued for a long period of time, and viscosity change of ink is suppressed or prevented and it is held uniformly [ the viscosity of ink ], or almost uniformly. [0074] From the above result, even if it is composition in usual water metallic ink, the stability of viscosity with the passage of time can be raised by the easy method of setting pH of ink to 8.0-10. If pH stabilizer is used especially, the stability of the outstanding viscosity with the passage of time can be made to hold over a long period of time.

[Effect of the Invention] Since the water metallic ink constituent of this invention has specific pH, the stability of viscosity with the passage of time is excellent.

[Translation done.]